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A STUDY OF POLYMERS
CONTAINING SILICON-NITROGEN BONDS

Quarterly Progress Report for the Period
April 4, 1963 to July 3, 1963

To

GEORGE C. MARSHALL SPACE FLIGHT CENTER
National Aeronautics and Space Administration
Huntsville, Alabama

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Birmingham 5, Alabama

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Robert E. Burks, Jr. *encl*
Thomas W. Ray
Organic Section

(NASA)
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A STUDY OF POLYMERS CONTAINING SILICON-NITROGEN BONDS

I. PURPOSE AND STATUS OF THE PROJECT

Silicon-nitrogen compounds are being studied in an effort to obtain thermally stable materials that will be useful in the space program. This report covers the first quarter of the third year of the program.

Polymers with good thermal and chemical stability were made by heating N-trimethylsilylhexaphenylcyclotrisilazane and N,N'-bis(trimethylsilyl)hexaphenylcyclotrisilazane at 400-450°C, but they were rather brittle. They will be studied further in efforts to obtain high molecular weights and improve the physical properties.

The study of factors affecting hydrolytic stability was continued. The N-benzyl and N,N'-dibenzyl derivatives of hexaphenylcyclotrisilazane hydrolyzed very slowly even in dilute acid. They are among the most stable monomeric silicon-nitrogen compounds yet prepared. Octamethylcyclotetrasilazane was found to be considerably more stable than hexamethylcyclotrisilazane.

Attempts to prepare a highly aromatic silicon-nitrogen polymer with phenylene bridges between Si-N-Si units were only partially successful—the product contained an appreciable amount of oxygen. However, the product had attractive thermal stability when it was heated in thin films, and so investigation of it will be continued.

II. POLYMERIZATION OF SILYL DERIVATIVES OF CYCLIC SILAZANES

A. Discussion

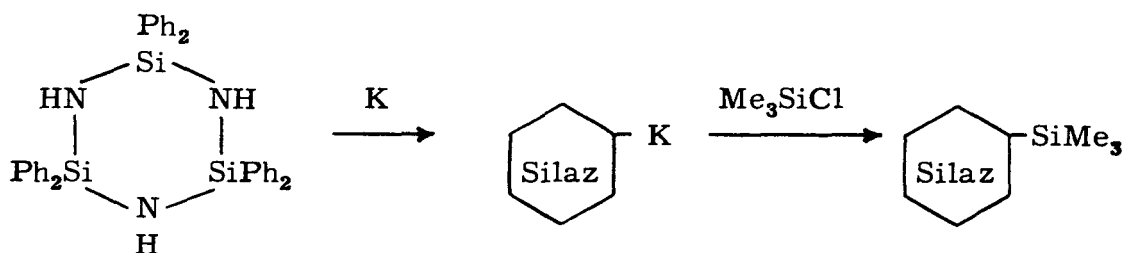
The N-trimethylsilyl derivatives of cyclic silazanes are being investigated to determine whether they can be used to make polymers with good thermal stability and other desirable properties. N-trimethylsilylhexaphenylcyclotrisilazane was polymerized by heating at 400-450°C to form a black, benzene-soluble polymer that softened only when heated above 450°C. A similar material was formed by heating N,N'-bis-(trimethylsilyl)hexaphenylcyclotrisilazane at 400°C. The preparation of the bis derivative proved to be difficult, because of the difficulty of making the second substitution. The first trimethylsilyl group was attached to the hexaphenylcyclotrisilazane ring relatively easily, but attempts to attach the second led to mixtures that were difficult to separate. Polymerization of the monosilyl substituted hexaphenylcyclotrisilazane will be studied in more detail to determine whether the reaction proceeds by a mechanism similar to the polymerization of hexaphenylcyclotrisilazane.

Hexaphenylcyclotrisilazane is known to polymerize at 420-575°C to form foamed, infusible solids. The object of our work is to modify hexaphenylcyclotrisilazane in a manner that will favor linear polymerization over cross-linking. Our plan was to replace the hydrogen of N-H groups with trimethylsilyl groups, so as to decrease the amount of hydrogen available for cross-linking. Apparently, polymerization as expected was not obtained. Instead the methyl groups reacted preferentially, but only a small amount of information has been obtained on the nature of the reaction.

The polymers obtained by heating the mono and bis(trimethylsilyl) derivatives of hexaphenylcyclotrisilazane at 400°C and at 450°C had high softening points and were not foamed. Hence, they represent progress toward a new type of silicon-nitrogen polymer. However, they were rather brittle, and so the desired increase in molecular weight was, apparently, not achieved.

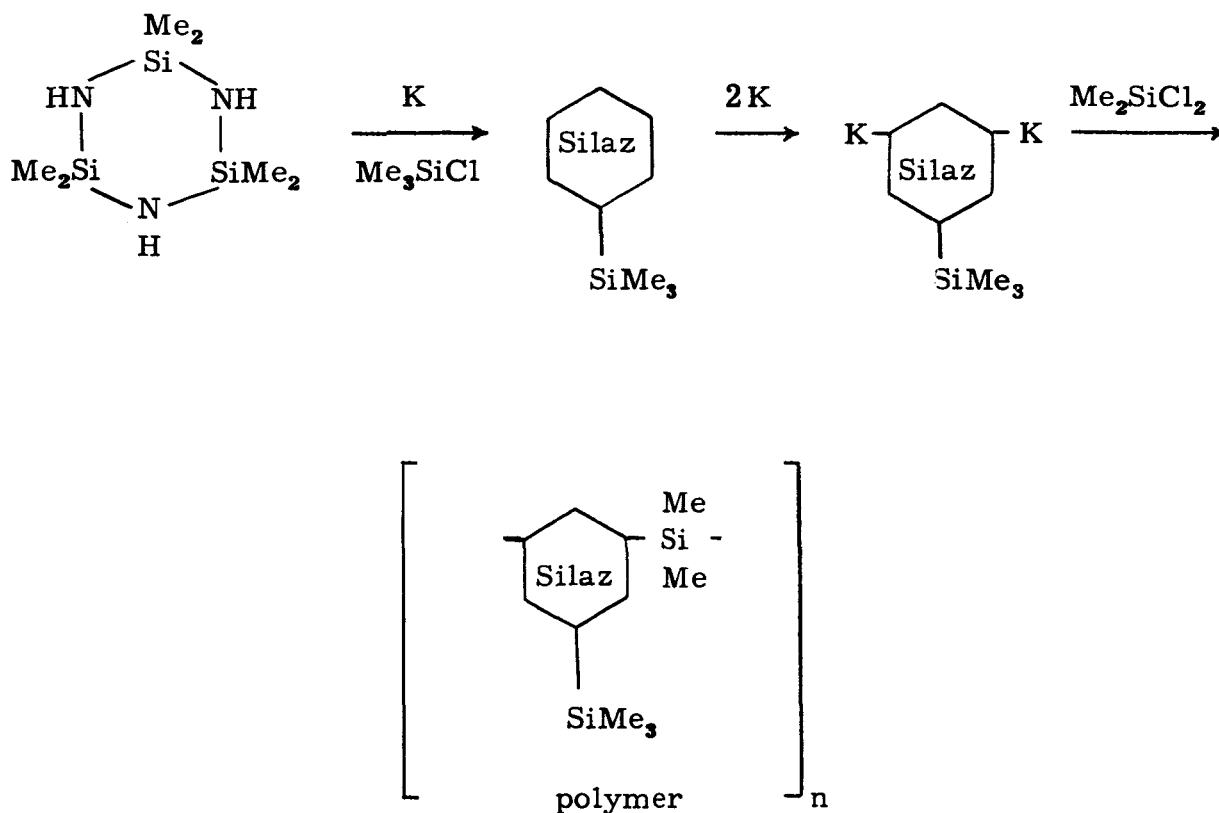
The N-benzyl derivatives of hexaphenylcyclotrisilazane are also being studied. The mono and bis benzyl derivatives were found to be comparable to the trimethylsilyl derivative in hydrolytic stability in that they were only slowly attacked by hydrochloric acid. Substitution at either one or two nitrogen atoms stabilized the entire ring.

Potassium proved to be useful in the preparation of derivatives of hexaphenylcyclotrisilazane;



but it did not react as readily with hexamethylcyclotrisilazane. Evidently the methyl groups on the silazane ring do not make the N-H groups sufficiently acidic for reaction with potassium. However, the addition of styrene caused the metalation of the ring to proceed satisfactorily. The use of styrene was suggested by Breed¹ and Goubeau.² The trimethylsilylhexamethylcyclotrisilazane is desired for future studies of polymerization by the following reactions:

1. L. W. Breed, R. L. Elliott, Quarterly Report 4, Army Project 593-32-002, Contract DA-23-072-ORD-1687, 15 October 1962.
2. V. J. Goubeau and J. Jimenez-Barbera, Z. anorg. allgem. Chemie **303**, 217-226 (1960).



B. Experimental Details

1. Polymerization of trimethylsilyl derivatives

a. Polymerization of N-trimethylsilylhexaphenylcyclotrisilazane

N-trimethylsilylhexaphenylcyclotrisilazane was prepared as described in the preceding annual report³ by treating hexaphenylcyclotrisilazane with potassium and trimethylchlorosilane. N-trimethylsilylhexaphenylcyclotrisilazane (0.5013 g, 0.755 millimole) was placed in a test tube that was swept

3. Annual Summary Report, Contract NAS 8-1510, George C. Marshall Space Flight Center, April 29, 1963, page 91.

with nitrogen, and the tube was capped with crimped aluminum foil. The tube was then inserted through a hole in the door of an oven at 400°C with the capped end protruding from the oven. The compound melted immediately. After 8 hours, it was a dark brown liquid; and after 23 hours it was a dark brown solid. The solid did not crack on being cooled. It weighed 0.3610 g. It did not melt or foam when heated over a Meker burner on a spatula that became bright red. However, when the spatula was heated with a blast lamp, the polymer melted, smoked, and then burned. The elemental composition was:

Found: C, 65.62%; H, 4.35%; N, 0.9%; Si, 21.0%;
Total, 91.87%

Theory for N-trimethylsilylhexaphenylcyclotrisilazane:
C, 70.53%; H, 6.22%; N, 6.33%; Si, 16.92%

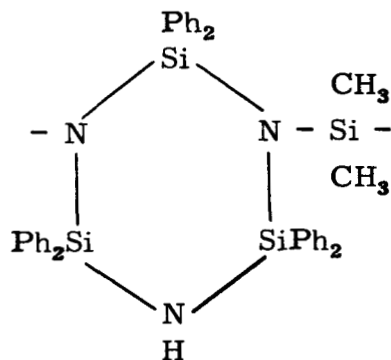
Nuclear magnetic resonance spectra showed that the ratio of the phenyl:trimethylsilyl:NH groups was 24:1:3.75 (theory for the starting material, 6:1:2). The low nitrogen analysis is questionable.

A second sample of N-trimethylsilylhexaphenylcyclotrisilazane (0.5262 g, 0.795 millimole) became solid after being heated at 450°C for 5 hours. It was a dark brown solid that weighed 0.3398 g and that behaved much like the sample obtained at 400°C. The elemental composition was:

Found: C, 62.96%; H, 4.63%; N, 5.75%; Si, 23.0%;
Total, 96.34%

Nuclear magnetic resonance spectra showed that the ratio of the phenyl:trimethylsilyl:NH groups was 28:1:9. The methyl groups had undergone no apparent change, and so those present were there as trimethylsilyl.

It is difficult to draw a simple formula that fits the analytical data on the polymer. The increase in silicon content combined with the large increase in phenyl groups as indicated by NMR eliminates a simple repeating group such as the following:



Theory: C, 70.43%; H, 5.75%;
N, 6.48%; Si, 17.34%

NMR: Ratio, phenyl : methyl : NH —
6 : 2 : 1

At 475°C, N-trimethylsilylhexaphenylcyclotrisilazane foamed partly and became solid in 4 hours. The entire mass was soluble in benzene. At 500°C a light tan foamed solid formed in 1.75 hours. It was not soluble in benzene.

Neither the 400° nor the 450° polymer was visibly affected by concentrated hydrochloric acid or concentrated sulfuric acid in 2 hours at room temperature. After being in each of the acids for 18 hours, there was no visible effect, except a slight cloudiness that was visible on the surface of the 450° polymer. Neither of the polymers was visibly affected by boiling in concentrated sulfuric acid for 10 minutes.

b. Polymerization of N, N'-bis(trimethylsilyl)hexaphenylcyclotrisilazane

N, N'-bis(trimethylsilyl)hexaphenylcyclotrisilazane, 0.1011 g (0.14 millimole), was placed in an 8-mm test tube which was then swept with nitrogen. The open end was capped by crimping aluminum foil over the top, and the bottom was inserted into an oven through a hole in the door. The capped end was left outside of the oven. After 5 hours at 400°C, the material in the tube was a dark brown liquid, but it had become perceptibly more viscous. At the end of 13 hours at 400°C, the sample was solid. At the end of 23 hours at 400°C, no additional visible change had occurred. The solid, vitreous, brown product was not soluble in benzene; and it would not melt on a spatula at red heat. It was not foamed. In the 23 hours at 400°C, the sample lost 35% of its weight.

2. Preparation of N-trimethylsilylhexamethylcyclotrisilazane

The N-trimethylsilyl derivative of hexamethylcyclotrisilazane was first prepared as described previously⁴ by the method of Breed.¹ The potassium method that had been used successfully with hexaphenylcyclotrisilazane was tried for preparing additional quantities of the silyl derivative of hexamethylcyclotrisilazane for our future work. In the first attempt, the potassium would not dissolve in hexamethylcyclotrisilazane. Consequently, the reaction was started again, and styrene was added to promote the reaction of potassium. The procedure was as follows:

In a 2-liter, 3-neck flask fitted with a condenser, thermometer, magnetic stirrer, and dropping funnel were placed 27.2 g (0.124 mole) of hexamethylcyclotrisilazane, 600 ml of dioxane, and 5.0 g (0.128 mole) of potassium. To this mixture, 10.0 g (0.096 mole) of styrene in 6 ml of dioxane was added. After 2 hours of refluxing all but a trace of potassium had dissolved. Trimethylchlorosilane, 13.43 g (0.124 mole) in 50 ml of dioxane was added dropwise, and the mixture was refluxed for another 2 hours. The resulting mixture was cooled and centrifuged, and the clear solution was distilled to obtain 16.8 g (45.6% yield) of N-trimethylsilylhexamethylcyclotrisilazane, n_D^{25} 1.4582. NMR spectra showed the correct ratio of methyl groups. A high-boiling viscous residue, 8.8 g, was also obtained.

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4. Annual Summary Report, Contract NAS 8-1510, George C. Marshall Space Flight Center, April 29, 1963, pages 83-88.

3. Preparation of N, N'-bis(trimethylsilyl)hexaphenylcyclotrisilazane

a. From N-trimethylsilylhexaphenylcyclotrisilazane

The procedure for preparation of N-trimethylsilylhexaphenylcyclotrisilazane used in this experiment is described in a previous report.³

In a 500-ml, 3-neck flask fitted with a magnetic stirrer, reflux condenser, thermometer, and dropping funnel were placed 60 ml of purified dioxane and 0.74 g (0.019 mole, 10% excess) of metallic potassium. Then 11.5 g (0.0173 mole) of N-trimethylsilylhexaphenylcyclotrisilazane dissolved in 100 ml of purified dioxane was added. The resulting solution was refluxed for 3 hours. At the end of this time, almost all the potassium had reacted. The solution was cooled, and 2.69 g (0.019 mole, 10% excess) of trimethylchlorosilane dissolved in 10 ml of purified dioxane was added over a 10-minute period. A white precipitate, presumably KCl, formed during the following 2 hours of refluxing. The reaction product was cooled and centrifuged. The precipitate, after being washed twice with dioxane, weighed 1.2 g (theory, 1.4 g).

The product was distilled to remove the dioxane, and the undistilled portion was dissolved in Skellysolve B.

Fractional recrystallization yielded 0.7 g (6.3% of theory) of crystalline product melting at 226-227°C. NMR spectra showed that the ratio of phenyl:trimethylsilyl:NH was 6:2:1 (theory, 6:2:1).

Found: C, 68.98%; H, 6.51%; N, 5.78%; Si, 19.1%

Calculated: C, 68.51%; H, 6.71%; N, 5.71%; Si, 19.07%

The molecular weight by vapor osmometry was 724 (average 728 and 720); theory 736.3. The determination was done by Galbraith Laboratories, Inc., Knoxville, Tennessee.

Attempts to repeat this preparation were not successful. In one attempt, the procedure just described was followed as closely as possible, but with only 7.8 g of N-trimethylsilylhexaphenylcyclotrisilazane and equivalent amounts of the other reactants. The product consisted of 1.4 g of crystals, m.p. 161-164°C; 0.5 g of crystals, m.p. 167-168°C; and 5.8 g of a pale yellow grease. In another attempt, styrene was added in an attempt to achieve better reaction of potassium. The product consisted of five fractions as follows:

1. 0.8 g, m.p. 169-170°C
2. 0.1 g, m.p. 166-167°C
3. 0.6 g, m.p. 154-157°C
4. 1.3 g, m.p. 333-334°C
5. 8.0 g, pale yellow grease

NMR spectra revealed no disubstitution product in the grease.

b. Additional attempts to prepare N, N'-bis(trimethylsilyl)-hexaphenylcyclotrisilazane

Additional attempts were made to prepare N, N'-bis(trimethylsilyl)hexaphenylcyclotrisilazane both by monosilylation of N-trimethylsilylhexaphenylcyclotrisilazane and by bis-silylation of hexaphenylcyclotrisilazane in one step. In addition, a mixture that was believed to contain both mono and bis derivatives was treated with potassium and trimethylchlorosilane in an attempt to increase the amount of the bis derivative to the point where it could be isolated. Only the reaction just described that started with pure N-trimethylsilylhexaphenylcyclotrisilazane successfully produced the pure bis derivative, and in that reaction the yield was only 6.3%.

4. Preparation of N-benzylhexaphenylcyclotrisilazane

In a 500-ml, 3-neck flask fitted with magnetic stirrer, reflux condenser, thermometer, and dropping funnel were placed 60 ml of purified dioxane and 1.09 g (0.0279 mole, 10% excess) of metallic potassium. The solution was heated until the potassium was well dispersed. Hexaphenylcyclotrisilazane, 15 g (0.0254 mole), dissolved in 120 ml of purified dioxane was added through the dropping funnel, and the resulting solution was refluxed for 3 hours. At the end of this time, all but a trace of the potassium had reacted. The solution was cooled, and 3.53 g (0.0279 mole) of benzyl chloride in 15 ml of dioxane was added. A white precipitate, presumably potassium chloride, formed during the following 6 hours of refluxing. The mixture was cooled, and the precipitate was filtered off. The residue, after being washed with dioxane and dried, weighed 1.8 g (theory for KCl, 2.08 g).

The dioxane was removed by distillation leaving an orange product that did not distill at a pot temperature of 145°C at 1.0 mm pressure. The product was dissolved in Skellysolve, and fractional crystallization yielded the following:

1. 2.4 g, m.p. 168-169°C
2. 0.6 g, m.p. 154-156°C
3. 7.3 g, m.p. 186-206°C
4. 5.0 g, viscous grease

15.3 g, total

NMR spectra of Fraction 1 indicated that it was N,N'-dibenzylhexaphenylcyclotrisilazane; the ratio of Si-phenyl to N-benzyl groups was 6:2 (theory for the N,N'-dibenzyl derivative, 6:2). The elemental composition of Fraction 1 was:

Found: C, 77.22%; H, 6.03%; N, 5.46%; Si, 10.4%

Calculated: C, 77.77%; H, 5.87%; N, 5.44%; Si, 10.92%

The yield was 15.7% of theory. The molecular weight is being determined.

NMR spectra of Fraction 2 indicated that it was N-benzylhexaphenylcyclotrisilazane; the ratio of Si-phenyl to N-benzyl groups was 6 : 1 (theory for the N-benzyl derivative, 6 : 1). The elemental composition was:

Found: C, 75.23%; H, 6.00%; N, 5.82%; Si, 11.8%

Calculated: C, 75.72%; H, 5.76%; N, 6.16%; Si, 12.36%

The yield was 3.9% of theory.

III. EVALUATION OF HYDROLYTIC STABILITY

A. Discussion

Hydrolytic stabilities of new silicon-nitrogen compounds are being determined in a study of the factors that affect hydrolytic stability. Rates of hydrolysis are compared by dissolving each compound in benzene or carbon tetrachloride and shaking the solution with water or dilute acid. Previous findings were discussed in the preceding annual report.⁵

The N-benzyl and N,N'-dibenzyl derivatives of hexaphenylcyclotrisilazane proved to be among the most stable silazanes to hydrolysis. They were comparable to the trimethylsilyl derivative of hexaphenylcyclotrisilazane. Attachment of the benzyl and the trimethylsilyl groups stabilized the entire rings and not just the portions of the rings close to the substituent group. Consequently, the stabilization evidently is more than a simple steric effect.

5. Annual Summary Report, Contract NAS 8-1510, George C. Marshall Space Flight Center, April 29, 1963, pages 19-46.

Octamethylcyclotetrasilazane was found to be more stable to hydrolysis than hexamethylcyclotrisilazane by a factor of 6. This difference was surprisingly great. It is becoming increasingly evident that the type of bonding in cyclic silazanes is not well understood. Before the stabilities of new compounds can be predicted, more information is needed on resonance and strain in the silazane rings.

B. Experimental Details

1. Method of measuring rate of hydrolysis

The method of comparing the rates of hydrolysis is described in an earlier report.⁵ Briefly, the procedure is to dissolve 0.5-5 milliequivalents of the silicon-nitrogen compound in 50.0 ml of carbon tetrachloride, shake the solution with 100.0 ml of water, and titrate the water layer periodically to determine the amount of ammonia or amine that appears. Compounds difficult to hydrolyze are compared by adding an amount of hydrochloric acid equivalent to the silazane.

Hydrolysis of N-benzylhexaphenylcyclotrisilazane was observed by dissolving 0.2303 g (1.014 milliequivalents) in 50.0 ml of carbon tetrachloride and shaking the solution with 100.0 ml of water for 176 minutes. No detectable further hydrolysis was observed after 18 minutes, when the amount hydrolyzed was approximately 3%. At this point, to conserve the limited amount of compound, acid hydrolysis was started with the same solution. An amount of acid equivalent to the silazane was added, and the hydrolysis was observed for 145 minutes. At the end of that period, the amount hydrolyzed was 33%. The data are plotted in Figure 1, and the results are given in Table I.

Detailed data are not presented for the hydrolysis of the N-benzyl compound in water because of the uncertainty of the distribution of benzylamine between carbon tetrachloride and water. However, there is no doubt that the extent of hydrolysis was small regardless of the distribution of benzylamine between solvent and water since the observed amount was only 3%. The uncertainty about distribution did not exist when acid was used.

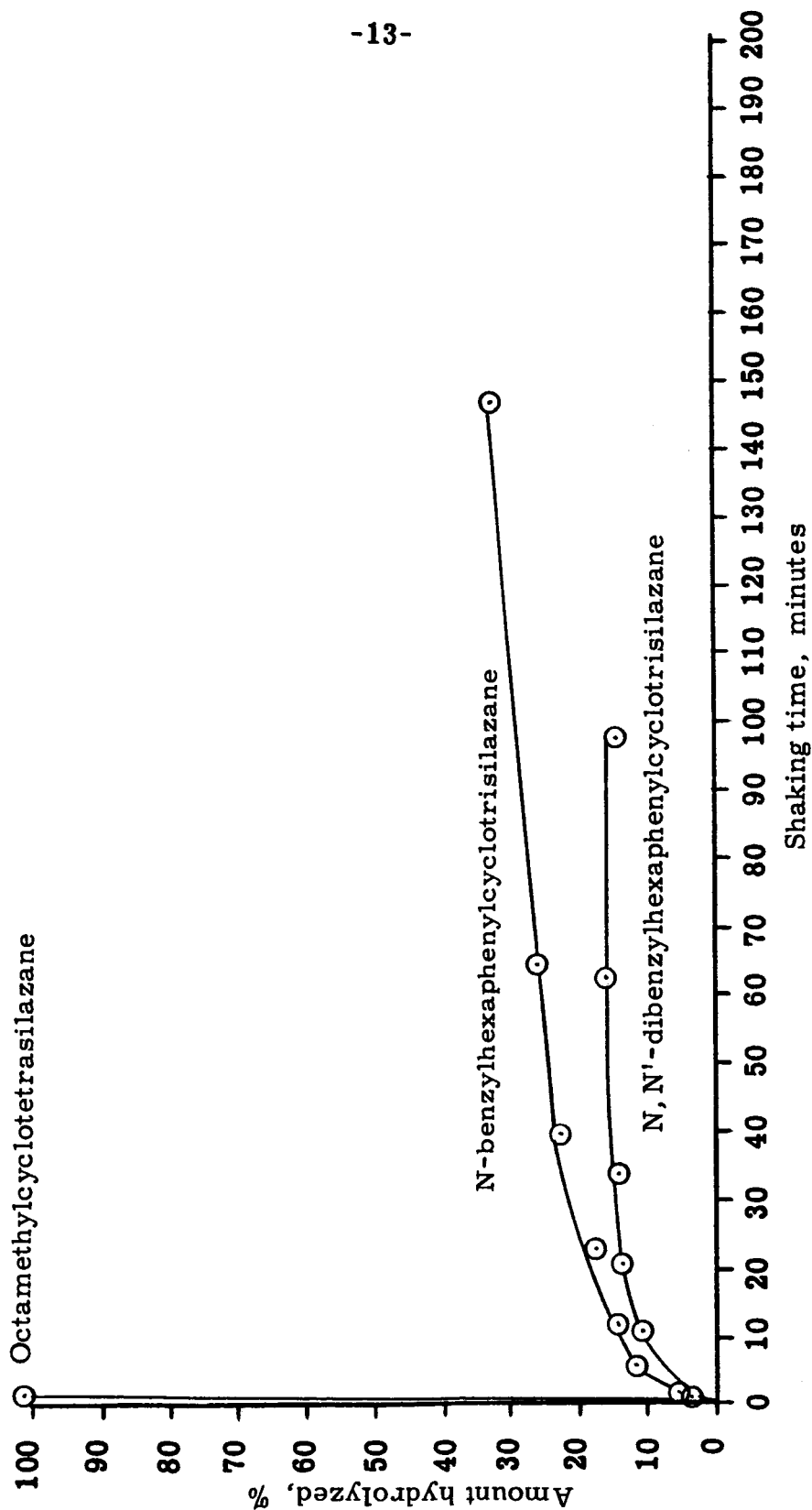


Figure 1. Hydrolysis in Carbon Tetrachloride with Hydrochloric Acid

Table I. Relative Rates of Hydrolysis

	CCl ₄ + H ₂ O		CCl ₄ + H ₂ O + HCl	
	Time for 25% hydrolysis, min	Hydrolysis in first 20 min. %	Time for 25% hydrolysis, min	Hydrolysis in first 20 min. %
N, N'-dibenzylhexaphenyl- cyclo-trisilazane			— *	13
N-Trimethylsilylhexaphenyl- cyclo-trisilazane			139	9
N-Benzylhexaphenylcyclo- trisilazane			60	18
Octamethylcyclotetrasilazane (average of two determi- nations)		3.8	<1	100
Hexamethylcyclotrisilazane	23	23	<1	100

* About 15% hydrolyzed in 100 minutes—progression of hydrolysis not detected after 30 minutes.

After the prolonged hydrolysis with acid, the carbon tetrachloride layer was evaporated, and 0.1817 g of solid, m. p. 127-131°C (original compound, m. p. 154-156°C) was recovered. The amount expected was 0.129 g representing the amount remaining after loss due to hydrolysis and the withdrawal of two samples of the organic solvent layer for titration.

Hydrolysis of N, N'-dibenzylhexaphenylcyclotrisilazane was observed by the same procedure with 0.1491 g (0.579 milliequivalent) of the silazane. Only 10% hydrolysis was detected in water in 205 minutes. Acid was added, and the hydrolysis was continued for 97 minutes. The hydrolysis with the acid was 15%. Evaporation of the carbon tetrachloride layer and recrystallization of the residue yielded 0.0768 g of the original compound, m. p. 163-166°C (original 168-169°C). The data are plotted in Figure 1, and the results are given in Table I.

Hydrolysis of octamethylcyclotetrasilazane was observed by shaking 0.3725 g (5.1 milliequivalents) with carbon tetrachloride and water. In 50 minutes, 6% was hydrolyzed. In a second experiment, 3% hydrolyzed in 60 minutes. In the first, the unhydrolyzed octamethylcyclotetrasilazane was checked by titration of the organic layer; and, in the second experiment, 84% was recovered by evaporation and identified by melting point. In acid, 99% hydrolyzed in 1 minute. The data from hydrolysis in acid are plotted in Figure 1, and the data from water are plotted in Figure 2. The results are given in Table I with data previously obtained on hexamethylcyclotrisilazane.⁶

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6. Annual Summary Report, Contract NAS 8-1510, George C. Marshall Space Flight Center, April 29, 1963, page 21.

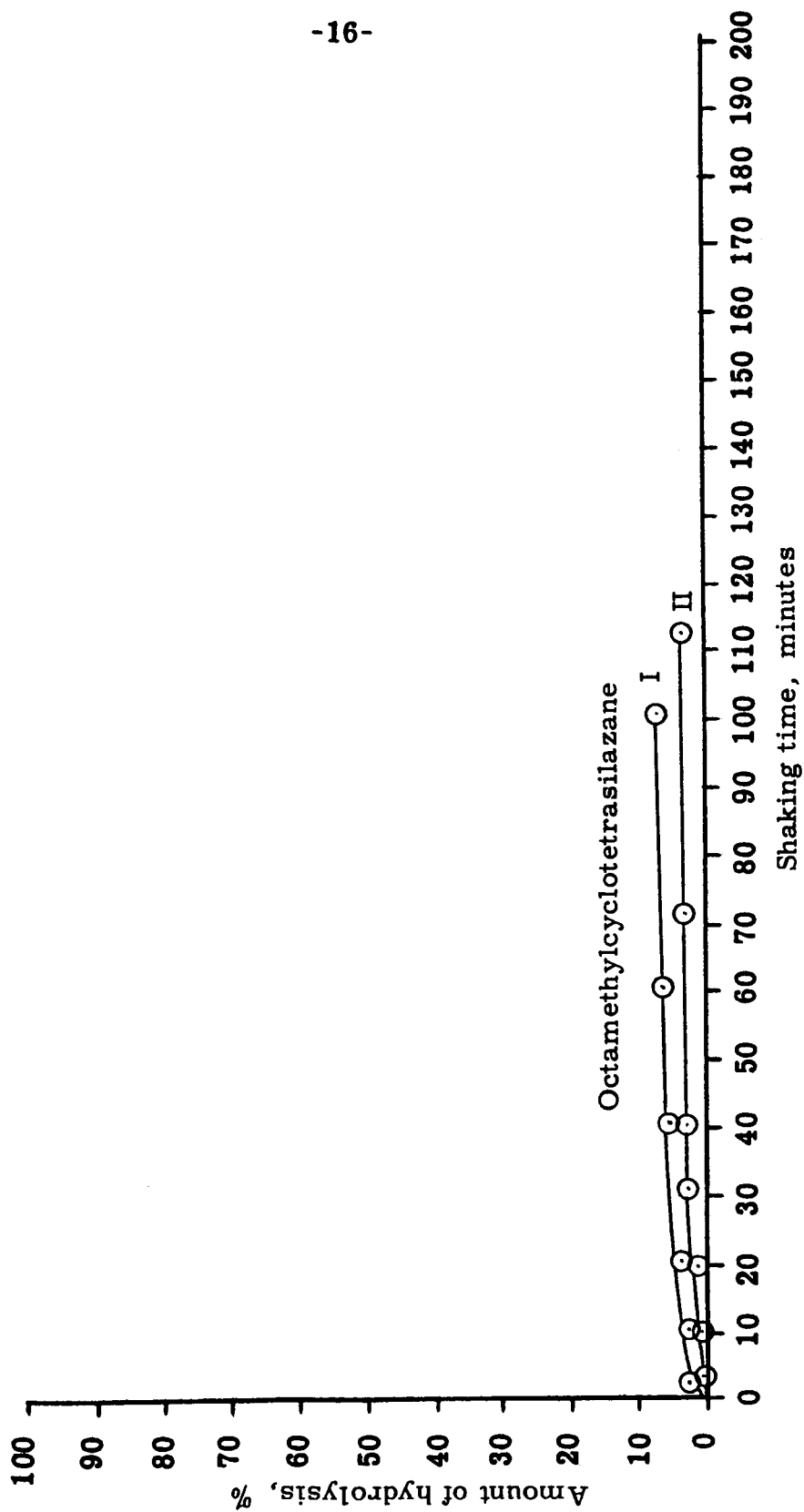


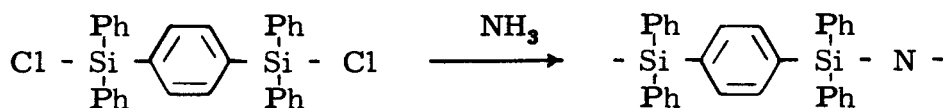
Figure 2. Hydrolysis in Carbon Tetrachloride and Water.

IV. SILICON-NITROGEN POLYMERS CONTAINING AROMATIC BRIDGES

A. Discussion

Efforts are being made to prepare silicon-nitrogen polymers from monomers having structures that favor the formation of linear polymers instead of cyclic compounds. In 1,4-bis(diphenylchlorosilyl)benzene the two functional groups are widely separated by a relatively stiff phenylene group. Consequently, cyclization would be inhibited in favor of linear chain formation. Furthermore, the phenylene unit is well known to be a highly stable structure, and 1,4-bis(diphenylchlorosilyl)benzene would be expected to form a silicon-nitrogen polymer with excellent thermal stability. Our previous work on these polymers is described in an earlier report.⁷

In our recent work, the method of Newing, Davis, and Towers⁸ has been used to prepare 1,4-bis(diphenylchlorosilyl)benzene, which was then treated with ammonia to form a silicon-nitrogen polymer.



1,4-bis(diphenylchlorosilyl)-
benzene

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7. Annual Summary Report, Contract NAS 8-1510, George C. Marshall Space Flight Center, April 29, 1963, pages 142-143.
 8. C. W. Newing, Jr., F. C. Davis, and R. S. Towers (Stauffer Chemical Company), Quarterly Progress Report 5, Contract NAS 8-1510.

Difficulty was encountered in purifying the dichloro compound, and the subsequent reaction with ammonia produced a silicon-nitrogen polymer that contained appreciable oxygen. Nevertheless, it had interesting thermal properties.

The polymer was a waxy solid that bubbled when it was heated on a spatula. After a short heating time followed by cooling, it passed through a viscous stage where long fibers could be pulled from the melt with a glass rod, but the fibers were brittle. Continued heating up to red heat, converted the polymer to a friable mass. Thermal stability appeared to be much better on a panel. When the polymer was spread on an aluminum panel and heated until smoking stopped, the fused mass puddled and did not form a smooth coating. A mixture of 9 parts of the polymer with 1 part of ethylenediamine silazane heated on a panel for an hour at 500°C formed a polymer that was tough and flexible when cooled. Even in areas where it was 1-2 mils thick, it did not crack off the panel when it was scratched with a sharp point, although it could be torn. Elemental analysis supported the value for neutral equivalent, indicating that the polymer contained considerable oxygen. In view of the promising properties, attempts to prepare the pure 1,4-bis(diphenylchlorosilyl)-benzene will be continued.

Information was recently obtained on the preparation of 1,4-bis-(dimethylchlorosilyl)benzene^{9, 10} by a method slightly different from that of Newing, Davis, and Towers⁸, and it will be used in attempts to prepare a purer phenyl compound.

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9. E. G. Rochow and D. Kummer, Report on Contract Nonr-1866(13), Office of Naval Research, January, 1963.
 10. M. Sveda, U. S. Patent 2,561,429 (to E. I. du Pont de Nemours and Company, Inc.), July 24, 1951.

B. Experimental Details

The attempt to prepare 1,4-bis(diphenylchlorosilyl)benzene was carried out as follows: In a 3-liter, 3-neck flask fitted with a stirrer, reflux condenser, thermometer, and dropping funnel were placed 29.2 g (1.2 mole) of magnesium turnings and 300 ml of tetrahydrofuran. To this was added dropwise, 141 g (0.6 mole) of p-dibromobenzene that had been dissolved in tetrahydrofuran. The resulting mixture was refluxed 2 hours and then left over the weekend in a nitrogen atmosphere. The solution of the Grignard Reagent was added over a period of 2 hours to 303 g (1.2 mole) of diphenyldichlorosilane in 500 ml of tetrahydrofuran. The mixture was stirred for 3 hours and left in a nitrogen atmosphere overnight. The tetrahydrofuran was removed by rapid distillation, and the residue was stirred with 1800 ml of heptane. The liquid suspension was filtered with all of the apparatus in a polyethylene bag filled with nitrogen. The colorless filtrate was cooled in dry ice and then left overnight in a refrigerator, whereupon a few crystals formed. These were filtered off in a nitrogen atmosphere and were found to have a neutral equivalent of 504 (theory, 256). Three successive recrystallizations reduced the neutral equivalent to 384. The product weighed 10.7 g (3.5% yield).

The crystalline product, presumably 1,4-bis(diphenylchlorosilyl)benzene, was treated with ammonia in the following manner: In a 1-liter, 3-neck flask fitted with stirrer, reflux condenser, thermometer, and gas inlet tube were placed 200 ml of benzene and 10.7 g (0.0209 mole) of crude 1,4-bis(diphenylchlorosilyl)benzene. Ammonia was passed through the gas inlet tube for 9 hours, and a positive pressure of ammonia was maintained on the reaction with the aid of a balloon on top of the condenser. The Beilstein Test for halogens was negative. The solution was refluxed for 3 hours. After being cooled, the reaction mixture was filtered to remove ammonium chloride. The benzene was distilled off; and the residue, 7.2 g, was a creamy, waxy solid. The elemental composition was:

Found: C, 73.61%; H, 5.34%; N, 2.39%; Si, 11.5%

Calculated for $-\text{Si}(\text{Ph})_2-\text{C}_6\text{H}_4-\text{Si}(\text{Ph})_2\text{NH}-$: C, 79.07%; H, 5.53%;

N, 3.07%; Si, 12.33%

V. ANTICIPATED WORK

Work will be continued on the use of alkali derivatives of silazanes as intermediates for preparation of silicon-nitrogen polymers. Work will be started with the alkali intermediates to make unsymmetrical derivatives of cyclic silazanes that may have lubricating properties.

Work will be continued on the preparation of silicon-nitrogen polymers with aromatic bridges by treating 1,4-bis(diphenylchlorosilyl)benzene with ammonia and methylamine.

An investigation will be started of the polymerization of cyclic silazanes at high temperatures in sealed vessels. The procedure to be tried is described in a patent,¹¹ but it has not yet been tried in this laboratory.

VI. TIME EXPENDITURE


The time expenditure during the quarter covered by this report was 1792 man-hours.

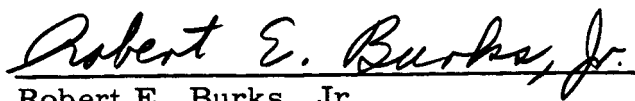
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11. S. J. Groszos and J. A. Hall, U. S. Patent 2,885,370 (to American Cyanamid Company), May 5, 1959.

ACKNOWLEDGMENTS


Mr. Robert E. Lacey, Senior Chemical Engineer, has assisted with the planning and interpretation of the laboratory work. Miss Mary Ann Fromhold, Assistant Chemist; Mr. William L. Mayfield, Research Technician, Mr. Howard A. Kirk, Research Technician; Mr. Franklin D. Alexander, Research Technician; Mr. Charles L. Christy, Jr., Chemical Technician; and Mr. Jerald T. LeBlanc, Laboratory Helper, assisted with the laboratory work.

Submitted by:


Thomas W. Ray
Organic Section


Robert E. Burks, Jr.
Head, Organic Section

Approved by:


C. E. Feazel, Head
Physical Sciences Division

Birmingham, Alabama
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PROGRAM PLANNING CHART

	Allotted time, man-hours	1963												1964		
		April	May	June	July	August	September	October	November	December	January	February	March			
A. Synthesis of Polymers and Compounds with Desired Characteristics																
1. Lubricants - unsymmetrical derivatives of cyclic silazanes (see B. 1. b)	400				X	X										
2. Elastomers - silyl derivatives of ethylenediamine (see B. 7)	400															
3. Structural plastics	900	X	X	X	X	X										
B. Study of the Chemistry of Silicon-Nitrogen Compounds																
1. Metallation of silylamines as a method of synthesis	500	X	X	X	X											
a. Polymers	-															
b. Lubricants (see A. 1)	900						X	X	X	X	X	X	X			
c. Organometallics																
2. Polymerization of cyclic silazanes at high temperatures and pressures	280				X	X										
3. Condensation polymerization of silylamines with difunctional aromatic compounds	280							X	X	X	X	X	X			
4. Steric factors to inhibit cyclization	900						X	X	X	X	X	X	X			
5. Polyethylenimine as a source of silicon-nitrogen polymers	400						X	X	X	X	X	X	X			
6. Properties of methyldiisobutylamine silazanes (see A. 2)	200						X	X	X	X	X	X	X			
7. Elastomers from ethylenediamine silazanes (see A. 2)	-															
8. Addition of silicon tetrafluoride to silazanes and amines	280								X	X	X	X	X			
9. Heats of combustion as indicators of aromaticity	420															
10. Polymers from methyldichlorosilane and silicon tetrachloride	420															
11. Silicon-nitrogen compounds with aromatic bridges	510	X	X	X	X	X										
12. Factors affecting hydrolytic and thermal stabilities	510				continuous											
C. Evaluation of Polymers (thermal, hydrolytic, and radiation stability)	510				continuous											
D. Applications - Search for New Uses	510				continuous											
E. Heat Barriers	510				At time designated by NASA											
F. Preparation of Final Report	170															
	9000															X

Descriptions correspond to sections of Proposal 2186 - March 20, 1963.